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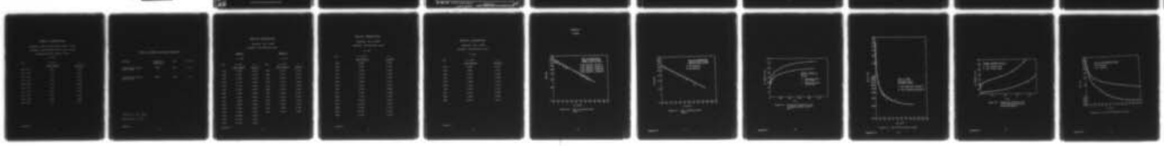

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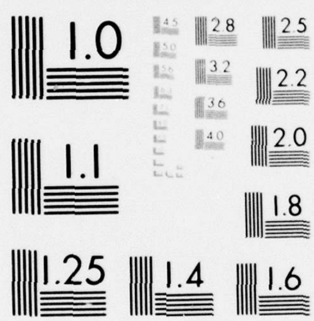
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EDGEWOOD ARSENAL CONTRACT REPORT

EC–CR–77020

GAS ADSORPTION BY ACTIVATED AND IMPREGNATED CARBONS

QUARTERLY PROGRESS REPORT

July 1976 to October 1976

by

P. J. Reucroft

C. P. Madhusudhan

G. B. Freeman

February 1977

UNIVERSITY OF KENTUCKY

Lexington, Kentucky 40506

Contract DAAA15–74–C–0163

DEPARTMENT OF THE ARMY

Headquarters, Edgewood Arsenal

Aberdeen Proving Ground, Maryland 21010

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Superactivated carbon 1	ASC whetlerite	Dubinin-Polanyi equation
Superactivated carbon 2	Adsorption	Physical adsorption
BPL activated carbon	Desorption	Chemisorption
Carbon tetrachloride	Water vapor	Hysteresis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

In the period reported, equilibrium adsorption isotherms have been measured for carbon tetrachloride on superactivated carbons 1 and 2 and water vapor on BPL activated carbon and ASC whetlerite carbon. Physical adsorption accounts for the obtained results and chemisorption effects were absent. W_0 values for superactivated carbons 1 and 2 were 0.82 $cm.^3 gm.^{-1}$ and 0.66 $cm.^3/gm.^{-1}$, respectively.

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PREFACE

The work described in this report was authorized under Contract No. DAAA 15-74-C-0163, Task 1W762710A09501, Gas Adsorption by Activated and Impregnated Carbons. The work described covers the period from 9 July 1976 to 8 October 1976.

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CONTENTS

RESEARCH PROGRESS DURING THE PERIOD

I. INTRODUCTION

In this period, carbon tetrachloride equilibrium isotherms were determined for two superactivated carbons, supplied by Edgewood Arsenal, and studies were initiated on the adsorption of water vapor by the BPL activated and ASC whetlerite carbons investigated previously.[1] The latter investigations are part of a program to determine the adsorption of binary mixed vapors by activated and impregnated carbons, when water vapor is one component in the mixture. The studies will be extended to assess equilibrium adsorption behavior under conditions where (a) the carbon is exposed to a mixture of the vapors, (b) the carbon is exposed first to component (A) and then to component (B) without removing adsorbed A, and (c) the carbon is exposed first to component (B) and then to component (A) without removing adsorbed (B).

II. ADSORPTION OF CARBON TETRACHLORIDE ON SUPERACTIVATED CARBONS

Superactivated carbon (Lot E 70-80) was designated superactivated carbon 1 and superactivated carbon (Lot E 70-90) was designated superactivated carbon 2. Adsorption and desorption data for both of these carbons were compiled with carbon tetrachloride serving as the adsorbate.

The outgassing procedure for both carbons consisted of heating the carbon to 400°C under 10^{-6} torr and vacuum pumping for 7 to 9 hours. After the sample had reached a constant minimum weight, the carbon was allowed to equilibrate with the ambient temperature, and CCl_4 vapor was introduced into the system. The mass of the sample and the vapor pressure were again allowed to equilibrate. These data points were recorded and subsequent isotherm points were then obtained either for the adsorption or the desorption process. At the end of an experimental run, the sample was again heated to 400°C under 10^{-6} torr for four hours, weighed and that mass compared to the initial minimum sample mass. Any adsorbate remaining after this process was attributed to chemically bound or chemisorbed material.

III. PRELIMINARY DETERMINATION OF WATER VAPOR ADSORPTION BY BPL ACTIVATED CARBON AND ASC WHETLERITE CARBONS

The experimental procedure followed for the superactivated carbons was the same as that used for the BPL activated carbon and ASC whetlerite carbon with water acting as the adsorbate of interest. The outgassing temperatures used were 150-200°C instead of 400°C. These preliminary results covered the relative pressure (P/P_0) range up to about 0.5.

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[1]P. J. Reucroft, C. T. Chiou and C. P. Madhusudhan, Quarterly Progress Reports 1-8, May 9, 1974 to April 8, 1976, Edgewood Arsenal Contract DAAA15-74-C-0163.

IV. RESULTS AND DISCUSSION

Isotherm data were plotted in the form of the Dubinin-Polanyi equation (figures 1, 2, 4, and 6):

$$\log W = \log W_0 - k\varepsilon^2$$

where W, W_0, k and ε have their usual meanings.[2] The isotherm data are also tabulated in the form of W vs. P/P_0, where P is the equilibrium pressure of adsorbate vapor and P_0 is the saturated vapor pressure of adsorbate liquid vapor (Tables 1-4, 6-8). In addition, figures 3 and 5 show conventional isotherm plots of W (volume adsorbed, c.c./g) vs. P/P_0.

The adsorption and desorption processes in superactivated carbon 2 reached equilibrium rapidly in comparison to other carbons investigated in the program. Carbon 2 showed a lower value of W_0 (0.66 cm^3g^{-1}) than did superactivated carbon 1, which had a W_0 value of 0.82 cm^3g^{-1}. Both superactivated carbons had virtually the same value of k, 2.74×10^{-8} $cal.^{-2}mole^2$ and 2.75×10^{-8} $cal.^{-2}mole^2$ for superactivated carbons 1 and 2 respectively.

There was no evidence of either hysteresis or chemisorption during adsorption-desorption runs in the case of carbon tetrachloride adsorbed by superactivated carbons 1 and 2.

The Dubinin-Polanyi plot of the water vapor adsorption by BPL activated carbon and ASC whetlerite carbon deviated a great deal from a straight line as shown in figures 4 & 6. Figure 5 shows that ASC whetlerite and BPL activated carbon displayed the same qualitative water adsorption properties. This behavior agrees with earlier work done on water vapor adsorption by graphite.[3] The ASC whetlerite activated carbon adsorbed significantly more water vapor than the BPL activated carbon at the same relative pressures. This may be explained by the greater affinity of water molecules for the impregnated metallic ions in the ASC whetlerite. Both carbons adsorbed far less water than previously studied organic adsorbates at the same relative pressures.[4] Figure 6 shows the relatively large adsorption hysteresis exhibited by both carbons examined. However after outgassing the sample subsequent to a data run there was no evidence of any chemisorption of water by either of the carbons.

Measurements of water vapor adsorption for the two carbons at pressures exceeding $P/P_0 = 0.5$ are currently in progress.

---

[2] P. J. Reucroft, W. H. Simpson, and L. A. Jonas, J. Phys. Chem., 75, 3526 (1971).

[3] G. J. Young, J. J. Chessick, F. H. Healey and A. C. Zettlemoyer, J. Phys. Chem., 58, 313 (1954).

[4] P. J. Reucroft, and C. T. Chiou, Fourth Quarterly Progress Report, January 1975 to April 1975, Edgewood Arsenal Contract DAAA15-74-C-0163.

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APPENDIX A

TABLES

Table A-1. Desorption Data

Adsorbate: carbon tetrachloride ρ(liquid) = 1.594

Adsorbent: superactivated carbon 1 (Lot E 70-80)

(Outgassing at 400°C under 10^{-6} Torr)

First Trial			Second Trial		
T = 24°C			T = 21°C		
P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3} g^{-1})	P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3} g^{-1})
2.82×10^{-3}	12.01	0.375	2.22×10^{-1}	0.77	0.745
2.38×10^{-3}	12.74	0.356	1.22×10^{-1}	1.52	0.710
1.88×10^{-3}	13.73	0.330	5.53×10^{-2}	2.86	0.648
1.59×10^{-3}	14.47	0.308	2.81×10^{-2}	4.35	0.581
1.29×10^{-3}	15.42	0.285	1.66×10^{-2}	5.73	0.531

Table A-1. Contd.

Adsorbate; carbon tetrachloride ρ(liquid) = 1.594

Adsorbent; superactivated carbon 1 (Lot E 70-80)

(Outgassing at 400°C under 10^{-6} Torr)

Third Trial

T = 23°C

P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3} g^{-1})
8.56×10^{-2}	2.10	0.734
3.83×10^{-2}	3.69	0.658
2.23×10^{-2}	5.02	0.601
1.39×10^{-2}	6.32	0.552
8.80×10^{-3}	7.76	0.506
5.84×10^{-3}	9.15	0.463
3.89×10^{-3}	10.66	0.420
2.76×10^{-3}	12.00	0.387
1.88×10^{-3}	13.62	0.356
1.45×10^{-3}	14.79	0.326

Appendix A

Table A-2. Adsorption Data

Adsorbate: carbon tetrachloride ρ(liquid) = 1.594

Adsorbent: superactivated carbon 1 (Lot E 70-80)

(Outgassing at 400°C under 10^{-6} Torr)

$T = 24°C$

P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3} g^{-1})
1.39×10^{-3}	15.05	0.295
2.36×10^{-3}	12.75	0.348
5.12×10^{-3}	9.70	0.439
1.81×10^{-2}	5.60	0.572
9.93×10^{-2}	1.86	0.737
1.78×10^{-1}	1.03	0.784

Appendix A

Table A-3. Adsorption Data

Adsorbate: carbon tetrachloride ρ(liquid) = 1.594

Adsorbent: superactivated carbon 2 (Lot E 70-90)

(Outgassing at 400°C under 10^{-6} Torr)

T = 24°C

P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3} g^{-1})
1.46×10^{-3}	14.74	0.231
3.35×10^{-3}	11.25	0.311
8.36×10^{-3}	8.01	0.396
2.68×10^{-2}	4.60	0.493
9.33×10^{-2}	1.98	0.587
1.94×10^{-1}	0.94	0.623

Table A-4. Desorption Data

Adsorbate: carbon tetrachloride ρ(liquid) = 1.594

Adsorbent: superactivated carbon 2 (Lot E 70-90)

(Outgassing at 400°C under 10^{-6} Torr)

T = 24°C

P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3} g^{-1})
8.78×10^{-2}	2.06	0.587
4.63×10^{-2}	3.28	0.540
2.13×10^{-2}	5.15	0.480
1.31×10^{-2}	6.54	0.440
8.73×10^{-3}	7.81	0.409
5.91×10^{-3}	9.16	0.377
4.42×10^{-3}	10.22	0.350
3.16×10^{-3}	11.53	0.321
2.26×10^{-3}	12.92	0.295
1.65×10^{-3}	14.27	0.271

Table A-5. Summary of Adsorption Parameters

Adsorbent	Outgassing Temperature	W_0*	$k^{+} \times 10^8$
superactivated carbon 1 (Lot E 70-80)	400°C	0.82	2.74
superactivated carbon 2 (Lot E 70-90)	400°C	0.66	2.75

+units for k: $cal.^{-2}$ $mole^2$

*units for W_0: $cm.^3$ g^{-1}

Appendix A

Table A-6. Desorption Data

Adsorbate: H_2O $\rho = 0.998$

Adsorbent: BPL activated carbon

	Sample I			Sample II	
	T = 20°C			T = 22.5°C	
P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3}g^{-1})	P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3}g^{-1})
.4790	0.1836	0.0540	.4345	0.2391	0.0330
.3633	0.3479	0.0218	.3854	0.3113	0.0234
.2359	0.7090	0.0113	.3226	0.4389	0.0179
.1363	1.3479	0.0065	.2255	0.7625	0.0107
.0752	2.2772	0.0045	.1461	1.2739	0.0072
.0528	2.9459	0.0039	.0846	2.1023	0.0050
.0404	3.5040	0.0035	.0560	2.8737	0.0042
.0304	4.1494	0.0033	.0413	3.5136	0.0038
.0231	4.8340	0.0031	.0285	4.3806	0.0034
.0206	5.0887	0.0028	.0185	5.5054	0.0031
.0100	7.2276	0.0026	.0132	6.4804	0.0029
.0050	9.5645	0.0024	.0055	9.3806	0.0027
.0038	10.5090	0.0023			
.0016	14.0120	0.0021			
.0010	16.2811	0.0021			

Table A-7. Desorption Data

Adsorbate: H_2O ρ =0.998

Adsorbent: ASC whetlerite carbon

T = 22°C

P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3}g^{-1})
.3605	0.3562	0.0645
.2665	0.5950	0.0442
.1721	1.0554	0.0359
.1113	1.6540	0.0309
.0746	2.3137	0.0283
.0499	3.0863	0.0257
.0328	4.0137	0.0236
.0207	5.1836	0.0218
.0128	6.5447	0.0203
.0093	7.5224	0.0190
.0046	9.9245	0.0172
.0019	13.4257	0.0156
.0009	17.0512	0.0142
.0002	24.7692	0.0116
.0002	26.4750	0.0108

Table A-8. Adsorption Data

Adsorbate: H_2O ρ =0.998

Adsorbent: ASC whetlerite carbon

T = 21°C

P/P_0	$\varepsilon^2 \times 10^{-6}$ (cal.^{2} mole^{-2})	W (cm.^{3}g^{-1})
.4760	0.1892	0.1337
.3442	0.3901	0.0558
.1815	0.9973	0.0280
.0941	1.9123	0.0200
.0452	3.2818	0.0147
.0298	4.2155	0.0126
.0193	5.3178	0.0103
.0110	6.9432	0.0087
.0064	8.6897	0.0080
.0027	11.9664	0.0073

APPENDIX B

FIGURES

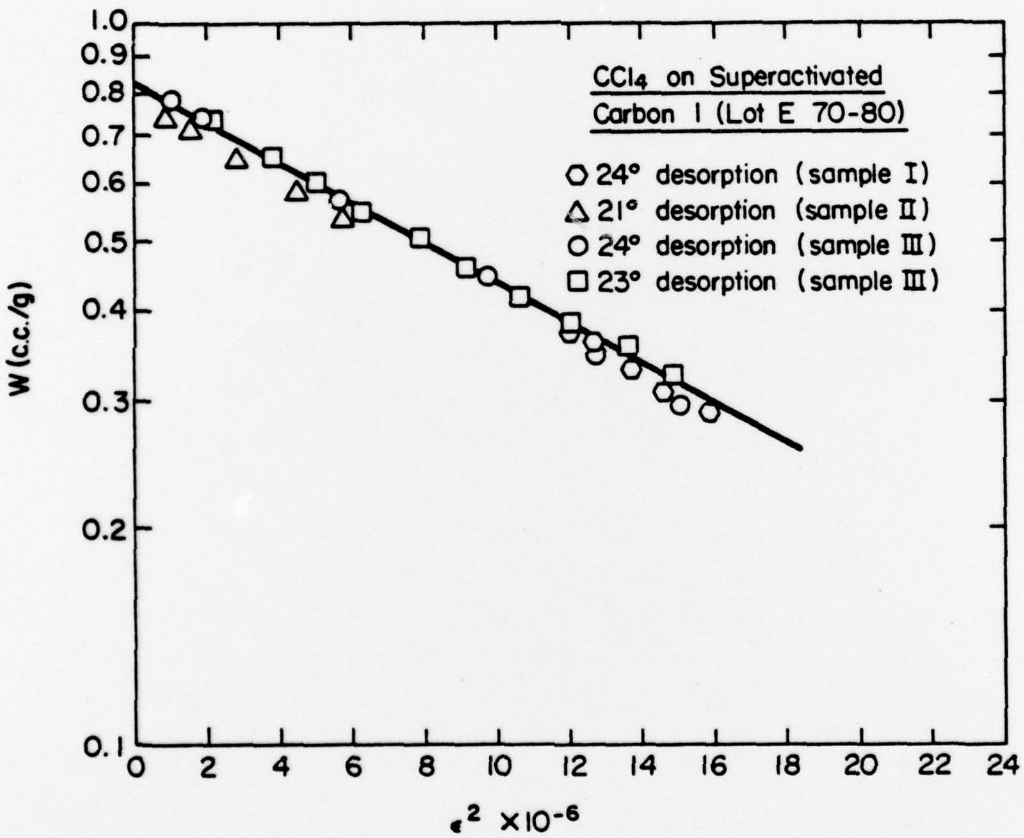

Figure B-1. CCl_4 on superactivated carbon 1

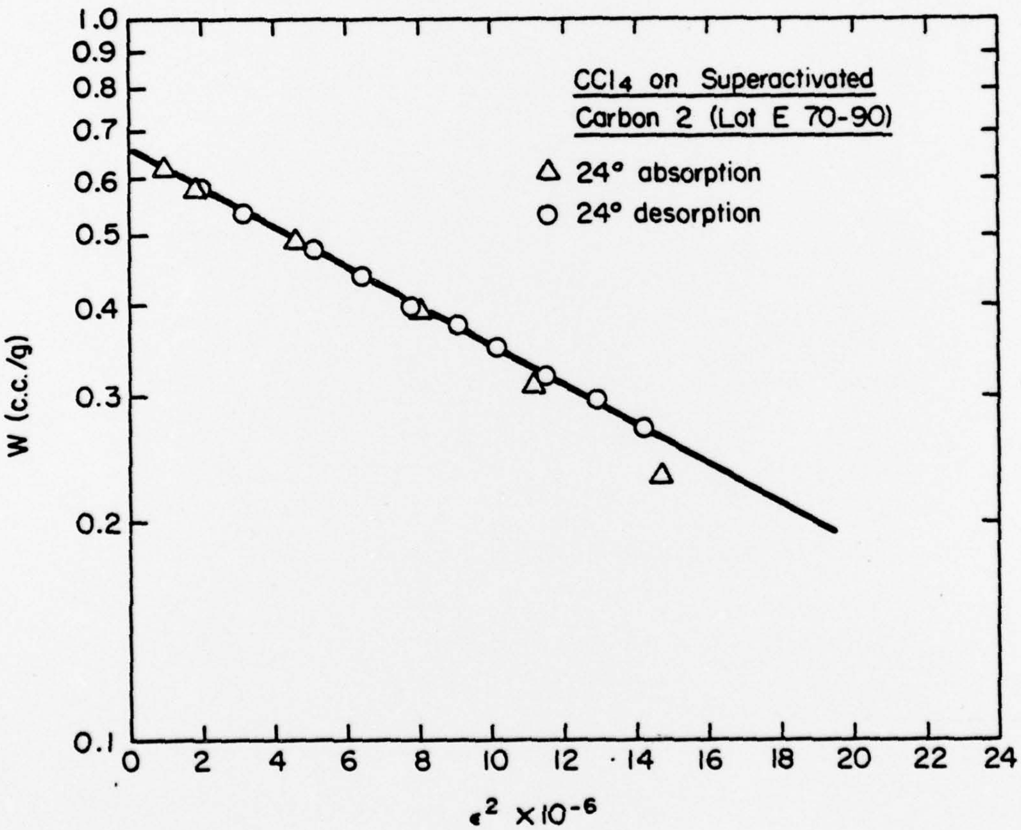

Figure B-2. CCl_4 on superactivated carbon 2

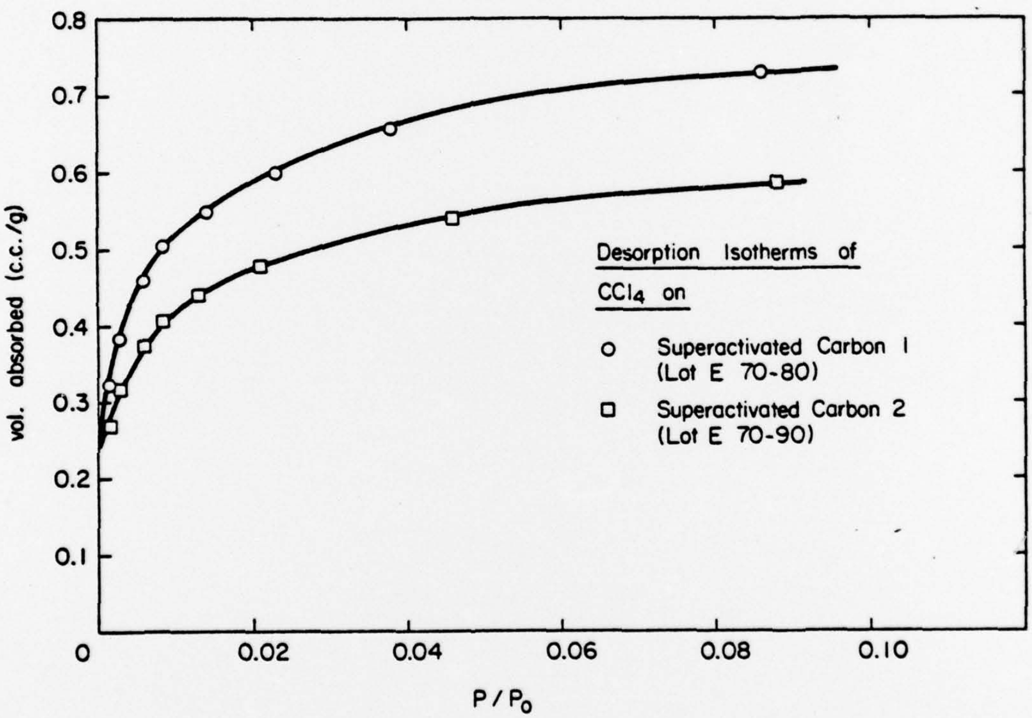

Figure B-3. Desorption isotherm of CCl_4 on superactivated carbons 1 and 2

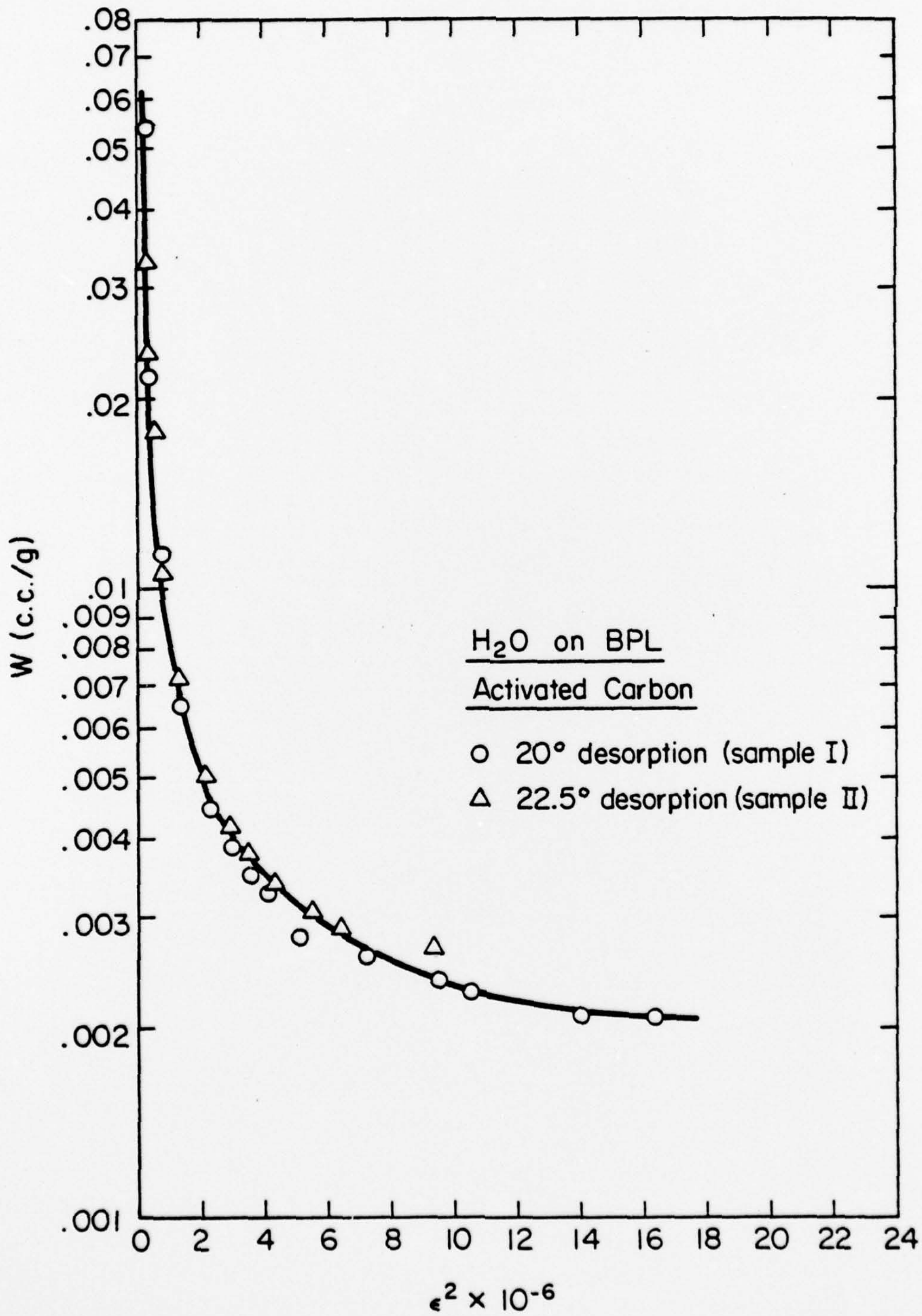

Figure B-4. H_2O on BPL activated carbon

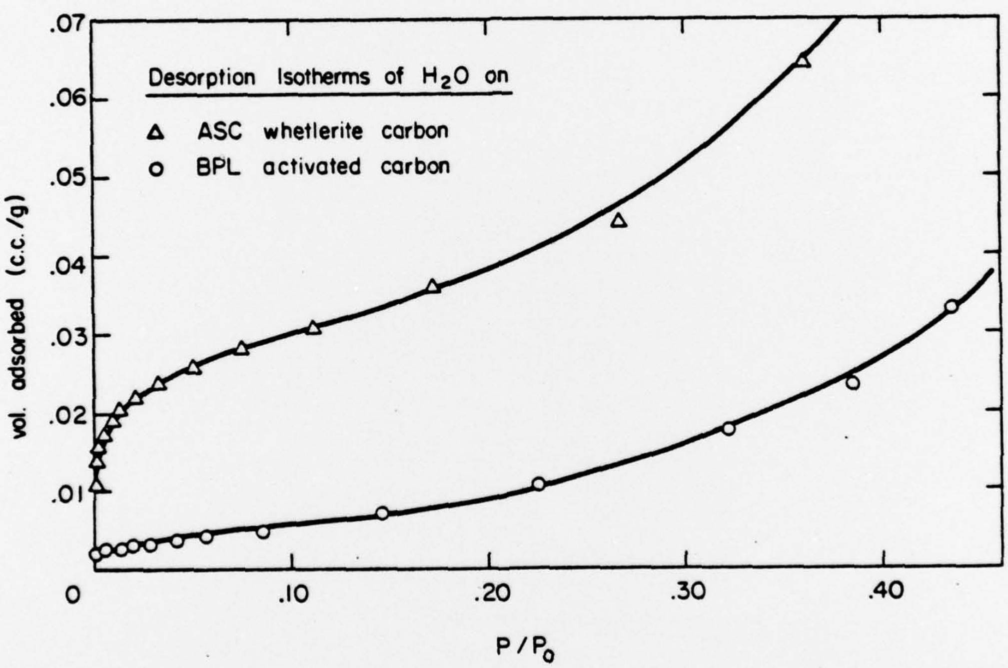

Figure B-5. Desorption isotherm of H_2O on ASC whetlerite and BPL activated carbons

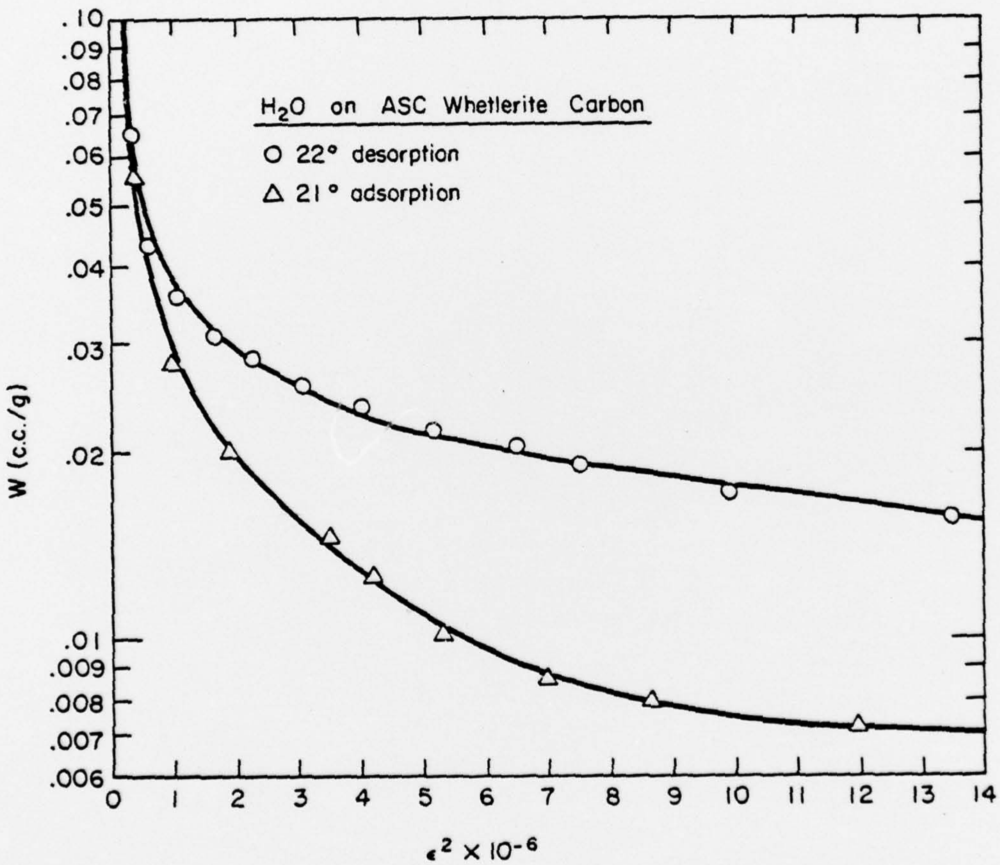

Figure B-6. H_2O on ASC whetlerite carbon